UTILIZATION OF WASTE

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USE OF METALLURGICAL SLAG IN THE COMPOSITION OF TILE MIXTURES

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The compositions of tile mixtures based on local clay and metallurgical slag are investigated. Using the mathematical planning method, the optimum mixture compositions for floor tiles are determined. The combined introduction of slag and cullet provides for a decrease in the firing temperature to 1050°C.

The material-saving technology of construction ceramics is based on replacing traditional materials brought from other regions with local clays and industrial waste. By volume, metallurgical slag and ash take a leading place among the industrial by-products, being next only to the mining industry wastes. Metallurgical slags are cooled melts of calcium and magnesium silicates and aluminosilicates. The yield of slag and ash resulting from solid fuel combustion is significant as well. Slag and ashes are distinguished by their diverse chemical and mineral composition [1].

Mine water purification waste and alkali-bearing waste resulting from concentration of polymetallic ores were suggested for use in the production of decorative tiles [2]. Combined introduction of up to 20% high-calcium and 30% alkali-containing waste made it possible to attain water absorption of 14.5% after firing at the temperature of 920°C. In [3], a composition for a floor tile mixture was developed using granulated cupola slag.

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TABLE 1

Raw material	Mass content, %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO + MgO	$Na_2O + K_2O$	V_2O_5	calcination loss
Novomoskovskii clay	78.8	12.6	4.0	2.8	0.7	–	3.5
Slag	26.6	3.0	0.4	63.1	–	0.5	2.5

Researchers from the Novomoskovsk Institute of the D. I. Mendeleev Chemical Engineering University have been studying for several years the utilization of industrial waste (chamotte dust, power plant ash) in production of building ceramics, specifically, floor tiles.

Based on the published data and preliminary research, testing of compositions based on local low-melting clay and mixed ferrovanadium slag which is a by-product of the steel-and-iron industry was proposed. The low content of fluxes (R_2O) in the slag and clay (Table 1) requires introduction of additional flux, such as glass cullet.

The mixtures were prepared by the slip method. The components were mixed in a material : balls : water ratio equal to 1 : 2 : 1. The suspension was dried in a drying cabinet. The obtained powder was compressed into samples under a specific pressure of 50 MPa. The samples were fired in a laboratory furnace with holding at the final temperature for 1 h. The quality of the samples was determined based on the water absorption, mean density, and linear shrinkage.

The water absorption of the pure clay samples fired at the temperature of 950 – 1000°C amounts to 11.5 – 12.0%, and virtually no shrinkage is observed. Intense sintering of the samples begins with the temperature of 1050°C, and after firing at 1100°C the water absorption decreases to 0.5%, but the sample surface becomes partially fused, which points to a narrow sintering interval.

The water absorption of the slag samples within the temperature interval of 950 – 1100°C remains at the level of 31 – 34%. The samples made of a mixture with 85% clay and 15% slag are only sintered to a level of water absorption below 4% at a temperature above 1050°C, and an increase in the firing temperature to 1100°C produces deformation and

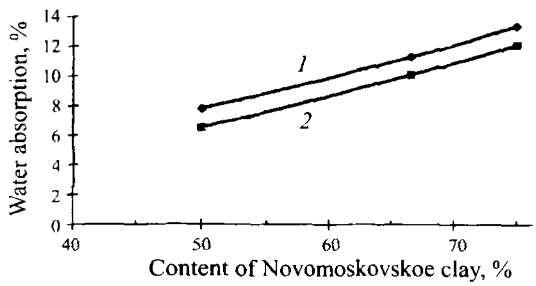

Fig. 1. Dependence of water absorption of samples on the Novomoskovskoe clay content for the firing temperatures of 900°C (*1*) and 1000°C (*2*).

TABLE 2

Mixture	Mass content, %		
	clay (X_1)	slag (X_2)	glass cullet (X_3)
1	90	0	10
2	60	30	10
3	60	0	40
4	70	20	10
5	80	10	10
6	70	0	30
7	80	0	20
8	60	10	30
9	60	20	20
10	70	10	20

fusion. Thus, addition of 15% slag to the local clay does not facilitate sintering and does not expand the sintering interval.

In order to increase the sintering interval by increasing the content of Al_2O_3 to 16 – 18%, it is expedient to use a combination of Novomoskovskoe and high-melting Veselovskoe clays. The ratio between the local clay and the high-melting clay varied from 1 : 1 to 3 : 1. At the same time, 20% cullet and 10% slag were introduced, in order to decrease the firing temperature.

It was found that at low firing temperatures (900, 1000°C) the water absorption of the samples increased with an increase in the amount of local clay in the mixture composition (Fig. 1), which is accounted for by the high sand content and the low flux content of the local clay. That is why a ratio between the Novomoskovskoe and the Veselovskoe clays equal to 1 : 1 was chosen for subsequent investigation.

In order to optimize the tile mixture composition, mathematical planning of the experiment was used, which consisted in plotting the "composition-property" diagrams in accordance with the simplex-grid plan. For our study we selected the cullet-slag-clay system composition region with the vertexes at points 1 (90, 0, 10), 2 (60, 30, 10) and 3 (60, 0, 40). The tile mixture compositions corresponding to the experimental plan matrix are shown in Table 2.

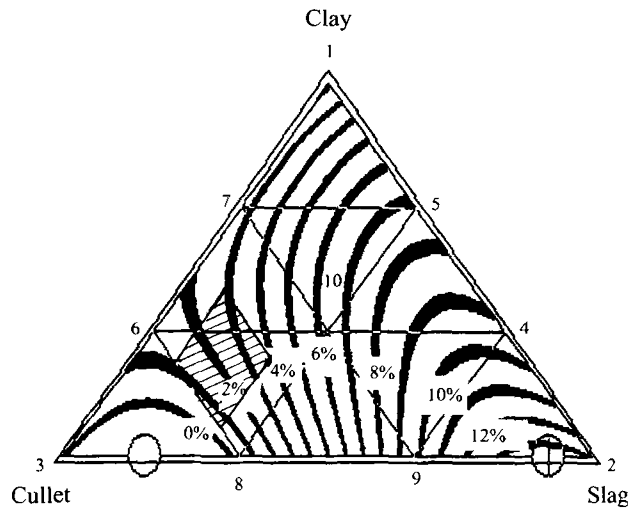

Fig. 2. Dependence of water absorption of samples on their composition at the firing temperature of 1050°C.

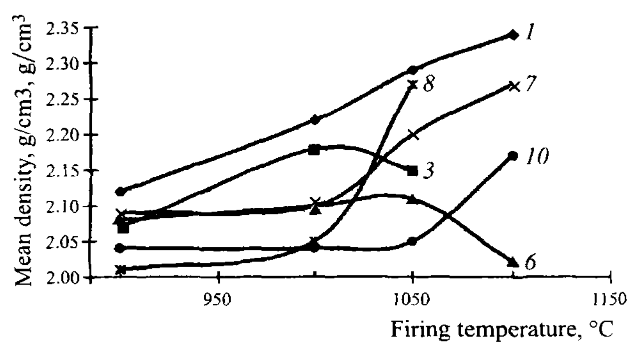

Fig. 3. Dependence of the mean density on the firing temperature. The numbers of the curves correspond to the numbers of the mixtures.

In the considered composition region the water absorption of the samples after firing at the temperature of 900°C does not attain the level required for floor tiles and is equal to 6.4 – 14.6%. After firing at the temperature of 1000°C, the water absorption below 4% was exhibited by the samples whose compositions are positioned near points *3* and *6* (Fig. 2). After firing at the temperature of 1050°C, the region of the sample compositions exhibiting water absorption below 4% is significantly expanded (Fig. 2). Moreover, the water absorption is largely determined by the cullet : slag ratio and sharply increases with an increase in the slag content.

After firing at the temperature of 1100°C, the samples of mixtures 3, 8, and 9 were fused, and the water absorption of the remaining samples was at the level of 0.1 – 0.6%. Accordingly, the fluxing effect of slag is demonstrated only starting with the temperature of 1100°C.

In order to determine the sintered state interval, the relationship of the mean sample density and the firing temperature was considered (Fig. 3) The samples of mixtures 1 and 7 intensely sinter within the temperature interval of 1000 – 1100°C without indications of overburning. The samples of mixtures 5 and 10 begin to sinter intensely at the temperature of 1050°C. The samples of mixtures 3 and 6 exhibit a decrease in density after firing at the temperatures of 1050 and 1100°C, respectively, which is the evidence of overburning.

Therefore, the mixtures with a high cullet content (3, 6, and 8) are excluded for having a narrow sintered state interval and a propensity toward deformation. The temperature of 1050°C is taken as the optimum temperature for firing of tile mixtures.

The optimum region of floor tile mixture compositions should be positioned between the curves reflecting water absorption of 0 and 4% (Fig. 2). For the purpose of slag utilization, the amount was restricted to 2 – 8%. Considering the data obtained with the regression equations, the following optimum mixture composition resulted (%): 62 – 74 clay, 24 – 30 cullet, and 2 – 8 slag.

Thus, introduction of slag up to 30 % ensures production of floor tiles at the firing temperature of 1100°C. A decrease in the firing temperature to 1050°C is possible if the slag content does not exceed 10% and the cullet content is increased.

After additional investigations are carried out to determine the abradability and to select the glazing, the optimum mixture composition can be recommended for production of floor tiles. The use of metallurgical slag will reduce the floor tile production cost and will contribute to partial solution of the environmental problems of the region.

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